

TANNING

The leather industry is divided into two broad categories—light and heavy leathers. Light leather includes shoe upper, lining, glove, garment, handbag, and novelty leathers and is made predominantly from light to medium weight cattlehides and from the skins of calf, goat, and sheep. Heavy leather includes sole, upholstery, bag, case, strap, and harness and is made from heavy cattlehides.

Light leathers are usually tanned with basic chromium sulfate referred to as "chrome" or "mineral" tanning. Some shoe lining and novelty leathers are tanned with "vegetable" tannins. Combinations of these tannages are used in some instances. Heavy leather is universally tanned with "vegetable" tannins which are complex mixtures of naturally occurring phenolic compounds.

Chrome Tanning. Basic chromium sulfate is used for chrome tanning. It is manufactured from chrome ore imported from Rhodesia, New Caledonia, and Turkey. It is applied in aqueous solution to skins "pickled" with sulfuric acid and sodium chloride to a pH of 2.0–2.5. In this pH range the chrome penetrates the skin or hide rapidly in a revolving drum. It reacts with the collagen when the skins are neutralized slowly to a pH of 3.5–4.0. The hydrothermal stability, shrink temperature, or "melting point" of the skin is raised to 90–100°C, and the protein is no longer susceptible to attack by bacteria.

The main mechanism of chrome tanning is usually considered to be the coordination of chromium to the carboxyl groups of collagen followed by the formation of secondary valences with the amino groups.

Vegetable Tanning. While there are many vegetable tannins, the most important ones are quebracho, chestnut, and wattle. Quebracho is extracted from the very hard and heavy wood of the quebracho tree which grows in Paraguay and Argentina. Chestnut is extracted from chestnut wood growing mainly in France and Italy. Wattle is extracted from the bark of black acacia trees, grown as a 7–10 year crop, mainly in south and east Africa.

Blends of vegetable tannins are always used in the manufacture of heavy leather in order to make use of the complementary properties of these tannins. Unlike chrome tanning, the initial pH of the liquor is in the range of 4.0–5.0 to permit penetration into hides that still contain calcium hydroxide from the unhairing. The pH is lowered gradually to 3.0–3.5 by countercurrent movement of stronger and more acidic liquors in a series of vats. Additional tanning is completed in drums with strong liquors.

The mechanism of vegetable tanning is the formation of numerous hydrogen bonds between the many phenolic hydroxyl groups of the tannins and the

oxygen and nitrogen atoms in collagen. Carboxyl groups occur in some vegetable tannins and form salt links. The relatively low hydrothermal stability of such leather is due to the weakness of the hydrogen bonds.

Alum, Formaldehyde, and Oil Tanning. These old tanning agents are used alone or in combination with chrome to produce specialty leathers such as white leather, glove leather and chamois. Alum is also used in the "tawing" of furs. They are relatively weak tanning agents and do not produce the high hydrothermal stability of chrome-tanned leather.

Zirconium Tanning. Basic zirconium sulfate is the only new mineral tanning agent. Its tanning action was discovered by I. C. Somerville in 1931. It is more expensive than chrome and is used for special purposes such as the manufacture of white grain and suede leather and for filling the flanks and shoulders of cattle "side" leather tanned with chrome for shoe upper leather.

While the mechanism of tanning is related to that of basic chromium sulfate, there is one striking difference, namely, that basic zirconium sulfate reacts with collagen at a much lower pH. For this reason it is applied to skins pickled to a pH of 1.0–1.5 at which appreciable tanning takes place even while the zirconium salt is penetrating the skin. The acidity is then neutralized gradually. At a higher pH the tanning action is so rapid that the grain is drawn and the center may be undertanned. However, zirconium can be applied to chrome-tanned leather at a pH of 2.5–3.5 without deleterious effect. Used alone, a higher amount of zirconium than chrome is required, partly due to the high molecular weight of the zirconium salt. Basic zirconium sulfate is a good filling and plumping agent. Unlike chrome, increasing amounts of zirconium increase the firmness of the leather. (See **Zirconium**)

Syntans. Synthetic tanning agents or syntans were developed by Edmund Stiasny beginning in 1911. Originally, both phenolsulfonic acid-formaldehyde, and naphthalenesulfonic acid-formaldehyde condensation products were made. For many years only naphthalene syntans were available partly because of the cost of phenol but also due to the shortcomings of the original phenolic syntans. Today a great many syntans are available for different purposes. They are usually referred to as auxiliary or replacement tans, depending upon their efficiency when used alone.

The naphthalene syntans are not tanning agents in the sense that they do not produce satisfactory leather when used alone. The "leather" is nonputrescible but is flat tinny and unsalable. However, these syntans serve many useful purposes. Their main use, for bleaching chrome-tanned skins for utility white

leather, was developed by Thomas Blackadder. The leather yellows readily, but this is reduced by a pigment finish. The sodium salts used on acidic chrome leather act as a dye-resist for acid dyes and permit greater penetration and uniformity of color, more particularly for pastel shades.

High quality phenolic syntans were eventually produced. They are based on phenolsulfone condensation products. The sulfone linkage, unlike the methylene bridge, confers substantial light resistance. Because of the large number of phenolic hydroxyl groups, these syntans are technically adequate to produce white leather when used as the only tanning agent. They are used with other tanning agents to produce such effects as textured grain leather with a deep, fine pattern.

World War II accelerated the search for an adequate replacement for vegetable tannins. This was developed by H. G. Turley and his associates. It is made by condensing phenol with formaldehyde and then sulfonating. It was "tailor-made" to produce sole leather with the same degree of tannage and yield of leather as vegetable tannins. In view of the complexity and high molecular weight of natural tannins, it is too much to expect sole leather made from a synthetic tanning material alone to be identical with that made from a blend of vegetable tans. The leather lacks the solidity and firmness desired in sole leather and imparted, for example, by chestnut extract. Its resistance to light is as low as that of quebracho. This substitute can be blended with vegetable tannins and, with processing adjustments, could be used as the only tanning agent in an emergency. Paradoxically, it is now used in larger volume for retanning chrome-tanned light leathers. The cost limits its use on sole leather generally to the extract wheel, following the yard tannage, to confer a desirable surface effect.

Melamine-Formaldehyde Tanning. Tanning with trimethylolmelamine was discovered before 1943 by W. O. Dawson. It is particularly interesting from a technical standpoint because it was the first organic tannage capable of producing leather that does not shrink in boiling water. In this respect it resembles an inorganic tannage. This is presumably due to the formation of numerous covalent crosslinks by a Mannich-type reaction. When too much is used the leather is weakened due in part to the properties of the resulting three-dimensional polymer and in part to too many crosslinks. When used alone, the leather is very white and light-fast. The tannage is somewhat astringent and expensive so that it is customarily used as a retannage of chrome-tanned leather for whites or for filling flanks.

Later it was found by W. Windus that it was not necessary to start with the preformed methylolmelamine. Melamine and formaldehyde can be added directly to depickled skins, and the tanning agent is formed *in situ*. The low solubility of the melamine is an automatic regulator of the rate of tanning which is convenient for uniform penetration of a skin.

Resin Impregnations. The first use of a resin for impregnation and tanning was developed by George D. Graves and J. S. Kirk in the late 1930's using a polymer of maleic anhydride and styrene. The skins are depickled to a pH of 4.0-5.0 and drummed with a water solution of the sodium salt of the polymer. The

skins are then acidified to precipitate the polymer. At this stage the shrink temperature is low, and the polymer can be washed out. It is permanently insolubilized by converting it to an aluminum, chrome, or zirconium salt. The resin does cause some complications in dyeing. However, when used alone or in combination with basic zirconium sulfate it produces a white suede with an excellent nap and a silky feel.

A more recent development is based on impregnation with polymers of urea or dicyandiamide and formaldehyde. These are dispersed with such agents as the sodium salt of a naphthalene syntan and then precipitated in the leather by acidification. The impregnant is white and is used to produce white leather or to improve the cutting value of the flanks of chrome-tanned side leather.

Resorcinol-Formaldehyde Tanning. It was discovered by W. Windus in 1946 that a synthetic tanning agent could be produced in the presence of the hide or skin in the customary dilute aqueous solution at room temperature, by using a very reactive phenol, such as, resorcinol or pyrogallol, with an aldehyde, such as formaldehyde or furfural. These compounds are added to pickled skins, and the pH is lowered to approximately 1.0 to increase the rate of reaction and tanning. A Mannich-type reaction between the low-molecular weight resorcinol-formaldehyde condensation product and the epsilon-amino group of the lysine residues of collagen was postulated.

In most respects the properties of the leather resemble those of a vegetable-tanned leather with one striking exception. The hydrothermal stability of resorcinol-formaldehyde-tanned leather is high. On skins it is easy to produce leather that does not shrink in boiling water.

Although the tannage is expensive it has been used to produce thousands of square feet of cattlehide survival moccasin (Mukluk) leather and goatskin shoe upper and handbag leather. It is used as a retannage on chrome-tanned sides to produce hockey gloves that dry out soft after repeated wetting. The tannage has also been applied to wool to produce a more durable papermakers' felt.

As a matter of scientific interest this *in situ* tannage has been extended to the use of tetrakis(hydroxymethyl)-phosphonium chloride with resorcinol in which the tanning must be carried out under mildly alkaline conditions. Commercial quality sheepskin leather has been produced.

Dialdehyde Tanning. The recent commercial availability of dialdehydes led to an investigation of their tanning action. It was found that glutaraldehyde, a five-carbon dialdehyde, was superior in its tanning action to other dialdehydes and also to formaldehyde. Although the maximum hydrothermal stability is only 85°C, the tannage is not reversed by washing or acidification. Leather tanned with glutaraldehyde alone or in adequate amounts with other tanning agents has improved perspiration resistance and stability to mild alkalis. This has led to its commercial use for the production of upper leather for work, sport, casual and nurses' shoes, and for shoe lining, shoe insoles, and hat sweat bands, usually in a combination tannage.

Glutaraldehyde can be used most conveniently as a retannage for chrome-tanned leather at an elevated

Dialdehyde Tanning

The tanning action of glutaraldehyde was announced simultaneously and independently in 1957 by E. M. Filachione and his associates and by L. Seligsberger. This five-carbon dialdehyde is markedly superior to formaldehyde in the stability of its combination with collagen and the properties it confers to leather. It is now widely used in basic research for the fixation of proteins.

Aldehydes are the only tanning agents that react most rapidly in slightly alkaline solution. When glutaraldehyde is used alone the pH is raised gradually from 4.0 to 8.5. The maximum hydrothermal stability is 85°C and the color of the leather is a light brown. Since essentially all light leather is chrome-tanned, tanners prefer to modify the leather by retanning with other tanning agents. This is the common method of using glutaraldehyde. Tanning is rapid at an elevated temperature and the normal pH of 3.5.

Glutaraldehyde enhances the perspiration resistance, alkaline stability and washability of leather. This had led to its application where these properties are in need of improvement. Uses include upper leather for work and nurses' shoes and hunting boots, lining leather for shoes and hat sweat bands, insole leather, and leather for golf, hockey and fliers' gloves and for garments. William F. Happich and his associates developed, by the use of a combination of glutaraldehyde and chrome, a sheepskin with the wool on (shearling) which is washable, thus making it practical for use as a medical pad by hospitals. A shearling is ideal for the prevention and cure of bed sores.

The mechanism of tanning is presumably the same as that for formaldehyde; namely, crosslinking of polypeptide chains through the epsilon-amino groups of the lysine residues. Spatial relationships and bifunctionality which permit greater crosslinking appear to account in large part for its superiority to formaldehyde.

References

The Chemistry of Tanning Processes. K. H. Gustavson, Academic Press, Inc., New York. 1956. Chemistry and technology of Leather, Vol. 2. F. O'Flaherty, W. T. Roddy and R. M. Lollar, Reinhold Publishing Corp., New York. 1958.

Journal of the American Leather Chemists Association, 52, 2 and 17 (1957); 59, 448 (1964).

Wallace Windus
Eastern Marketing and Nutrition
Research Division
Agricultural Research Service
U. S. Department of Agriculture
Philadelphia, Pennsylvania 19118